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OPTICAL CHARACTERIZATION OF EPITAXIAL $Ga_xIn_{1-x}As$ SUITABLE FOR THERMOPHOTOVOLTAIC (TPV) CONVERTERS

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ABSTRACT

A preliminary investigation of the optical characteristics of $Ga_xIn_{1-x}As$ epilayers is presented. $Ga_xIn_{1-x}As$ epilayers with x=0.465, 0.400, and 0.277 were prepared by metalorganic vapor-phase epitaxy (MOVPE) to represent a wide spectrum of TPV converter applications. Ellipsometric measurements, combined with various characterization techniques and multi-layer modeling, are used to extract n(λ) and k(λ) for these epilayers. The validity of the results was checked by using the experimentally determined optical constants to calculate expected reflectance, and then comparing this result against measured reflectance. Good agreement was obtained in all cases; larger differences were observed for samples having greater surface roughness. Suggestions for improving the optical constant determination procedure are given.

INTRODUCTION

The recent development of highly efficient low-bandgap PV converters has sparked a strong renewed interest in TPV technology. In particular, TPV converters fabricated at NREL from $Ga_xIn_{1-x}As$ epilayers have demonstrated promising performance [1]. To achieve converter bandgaps that are relevant to a wide spectrum of TPV applications (0.5–0.75 eV), a range of $Ga_xIn_{1-x}As$ compositions must be considered (x=0.22–0.47). To date, data regarding the wavelength-dependent optical constants n(λ) and k(λ) have not been available generally for the abovementioned compositional range. Optical constant data are key to the eventual optimization of TPV converters. For example, such data are necessary for modeling the quantum efficiency and for designing antireflection coatings.

OBJECTIVE

The principal objective of this work was to determine n(λ) and k(λ) for undoped epilayers of $Ga_xIn_{1-x}As$ spanning the previously mentioned range of x. A secondary objective was to investigate other characteristics of the epilayers that play a role in defining their overall optical properties.

EXPERIMENTAL APPROACH

$Ga_xIn_{1-x}As$ epilayers with x=0.465, 0.400, and 0.277 (hereafter referred to as samples 1, 2, and 3, respectively) were grown on InP substrates by atmospheric-pressure MOVPE for analysis. All epilayers were undoped, as this initial study was concerned with the intrinsic properties of the materials. Sample 1 is closely lattice-matched (LM) to InP, whereas samples 2 and 3 are lattice-mismatched (LMM). The LMM samples were grown by starting with a thin LM buffer layer of $Ga_{0.47}In_{0.53}As$. On this, a compositionally graded region is grown, where the Ga content is monotonically reduced, in a linear fashion, until the desired composition of $Ga_xIn_{1-x}As$ is reached. This region, called the continually graded layer (CGL), is included to mitigate the deleterious effects of LMM, and thereby to improve the surface morphology and material quality of the top layer. For the top layer, the composition is held constant. The top layers were intentionally grown at least 3-4 μm thick to make them "optically thick" for photon energies above the bandgap, so that a minimum of 95% of the radiation is absorbed. Cross-sections for these epistructures are shown in Fig. 1.

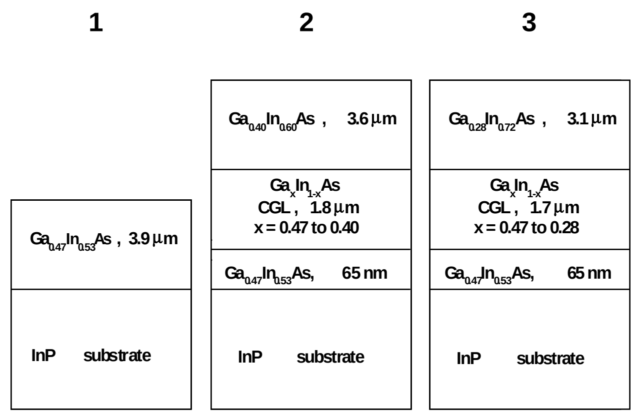

Fig. 1. Cross-sectional diagrams of the $Ga_xIn_{1-x}As$ epistructures showing nominal thicknesses and compositions of the component epilayers.

Initially, ellipsometric parameters of the samples were measured by scanning-wavelength ellipsometry. Properties of the samples were then studied by various techniques. Fourier transform-photoluminescence (FT-PL) measurements provided information about the bandgaps and material quality. Electron-probe microanalysis (EPMA) provided compositional information and helped establish a correlation between composition and bandgap. Atomic-force microscopy (AFM) was used to quantify the surface roughness induced by the LMM.

Ellipsometric data were then analyzed using nominal epilayer thickness values, derived from deposition rates, as inputs into a multi-layer optical computer model. The optical parameters n(λ) and k(λ) for the epilayers of interest were extracted using the multi-layer model and sophisticated algorithms.

Spectral reflectance measurements were also done on the $Ga_xIn_{1-x}As$ samples for wavelengths of 250-2000 nm, using a Varian Cary 5G spectrophotometer.

Finally, the optical constants determined by the multi-layer analysis were used to calculate the expected reflectance, which was compared against the measured reflectance.

RESULTS

Properties of $Ga_xIn_{1-x}As$ Epilayers

The room-temperature bandgaps for these materials can be best described by the equation relating the bandgap to the value of x in $Ga_xIn_{1-x}As$, at 300 K, given below [2]

$$E_g(x) = (0.555\,x^2 + 0.505\,x + 0.356)\text{ eV} \qquad (1)$$

Using this equation, and the previously mentioned values of x, the bandgaps of samples 1-3 are calculated to be 0.711, 0.647, and 0.538 eV, respectively.

FT-PL measurements were also performed to determine the bandgaps of the top layers in the structures directly. Room-temperature PL peak intensity energy values, corrected by a thermal factor of kT/2, gave bandgaps of 0.726, 0.651, and 0.556 eV, for samples 1-3, respectively. These are within 1.5% of the value generated using equation (1), for sample 1, and, similarly, within 4% for samples 2 and 3. The close agreement between these two methods of determining the bandgaps gives us a high degree of confidence in the measured values of x. The intensity of the PL signal for sample 1 was ~30 times greater than that for samples 2 and 3. These results show how the epilayer quality is affected adversely as the LMM increases. Full-width-half-maximum values of the PL peaks were 0.039, 0.050, and 0.042 eV for samples 1-3, respectively.

The AFM measurements showed an RMS roughness of only 2 Å for sample 1, which increased to 159 Å for sample 2, and further increased to 600 Å for sample 3. The LMM samples showed a cross-hatched surface structure, and the sample with the largest LMM showed a tendency to form surface pits, which may be due to a growth mode change from two- to three-dimensional [1].

Optical Constant Determination

Ellipsometric measurements were done using a scanning-wavelength ellipsometer with a rotating polarizer and fixed analyzer. Resulting measurements yield the parameters Psi, and Del, which are related to changes of the magnitude and the phase of reflected polarized light from the sample, respectively. Measurements were done on sample 1 for wavelengths of 400-1500 nm, and over a smaller range (700-1500 nm) for samples 2 and 3. Measurements were done at an angle of incidence of 70° for sample 1, and 72° for samples 2 and 3. The above values were chosen to maximize the sensitivity of the ellipsometric measurements [3].

Nominal thicknesses of layers in the epistructures were used as inputs into a multi-layer model. Because the samples were not etched at the time of measurement, a thin oxide layer was assumed to exist on the surface.

Optical constants were calculated for sample 1 by assuming that the surface layer was oxidized. The best fit to published data was achieved by using a 30 Å thickness of an assumed oxide (oxidized GaAs). The calculation incorporated the Hooke-Jeeves algorithm and used a five-parameter Lorentz-oscillator equation generated from referenced data [4]. The Lorentz oscillator equation closely approximates the spectral dependence of the dielectric function of semiconducting materials. Each oscillator corresponds to either a critical point in the band structure, or the broad background of the dielectric constant [5]. The parameters in the oscillator equation were allowed to vary for the best fit to the ellipsometric data.

Optical constants were calculated in a similar manner for the LMM samples 2 and 3. As for sample 1, the nominal epilayer thicknesses were used. In these two samples, the existence of a graded layer was accounted for in the model by varying the grade in 10 equal, compositional steps. These calculations incorporated the Global Levenberg-Marquardt algorithm [4], and used the same initial oscillator equation generated as in the LM case to start the data fit.

The results for n(λ) for all samples, along with two references (for $Ga_{0.47}In_{0.53}As$), are shown in Fig. 2. With the ellipsometric data modeled as above, n(λ) for sample 1 matched the two references very well.

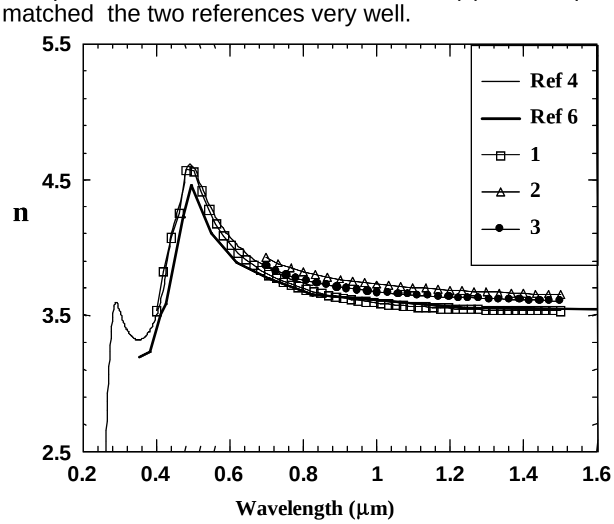

Fig. 2. n(λ) for samples 1-3, and references 4 and 6.

Results for samples 2 and 3 were not expected to be the same as for sample 1, because they have different values of x. We observed for samples 2 and 3 that n(λ) was slightly larger than that of sample 1, with sample 2 having the largest value. This seems to suggest that n(λ), beyond the critical points, increases marginally as x decreases. This is consistent with the trend that n follows if one considers the constituent binary components in $Ga_xIn_{1-x}As$. For example, at 1.03 μm, n(InAs)=3.61, and n(GaAs)=3.49 [8].

The k(λ) results for all samples, along with two references (for $Ga_{0.47}In_{0.53}As$), are shown in Fig. 3. As modeled, sample 1 matched the referenced data very well. As in the case of n(λ), mentioned above, the different values of x that were studied suggest that different k(λ) values should be obtained for each sample. The k(λ) results for samples 2 and 3 were slightly higher than for sample 1. The sample with the largest LMM, sample 3, was observed to have the largest value of k(λ) in this study.

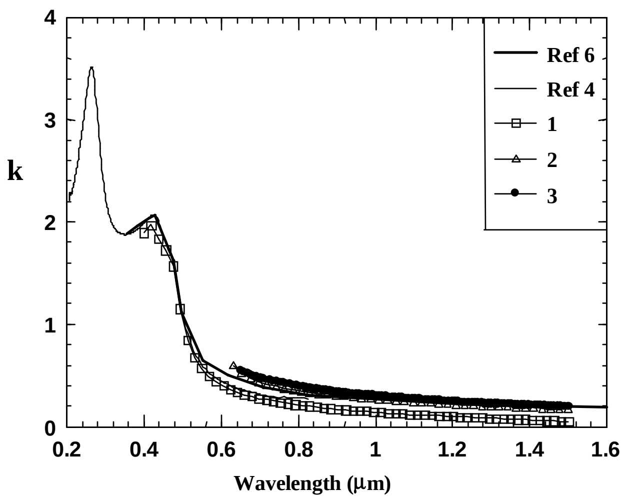

Fig. 3. k(λ) for samples 1-3, and references 4 and 6.

Modeled and Measured Reflectance

The optical constant results were used for calculating reflectance, and the results were compared to actual reflectance measurements. We found that the calculated reflectance for sample 1 matched the measured reflectance data to within 3%, as seen in Fig. 4.

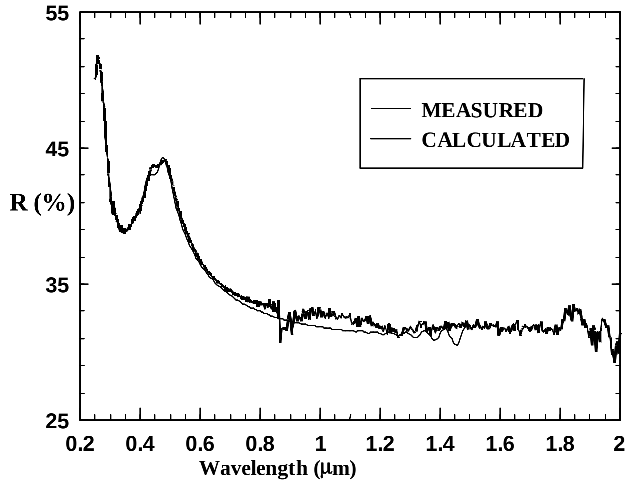

Fig. 4. Calculated and measured reflectance for sample 1.

Reflectance results for sample 2 differed by ~10% for the shorter wavelength range, to less than 3% for the longer wavelength range, as seen in Fig. 5. Here, the measured reflectance is lower than the calculated reflectance.

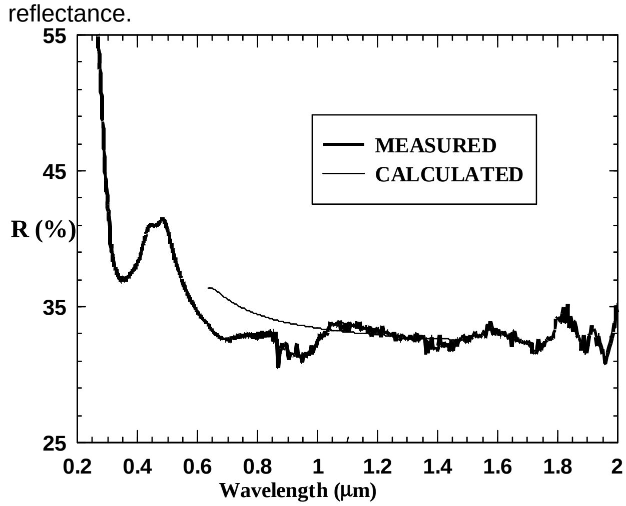

Fig. 5. Calculated and measured reflectance for sample 2.

Reflectance results for sample 3 differed by ~10% for the shorter wavelength range, to ~13% for the longer wavelength range, as seen in Fig. 6. As in the case for sample 2, the measured reflectance is less than the calculated reflectance.

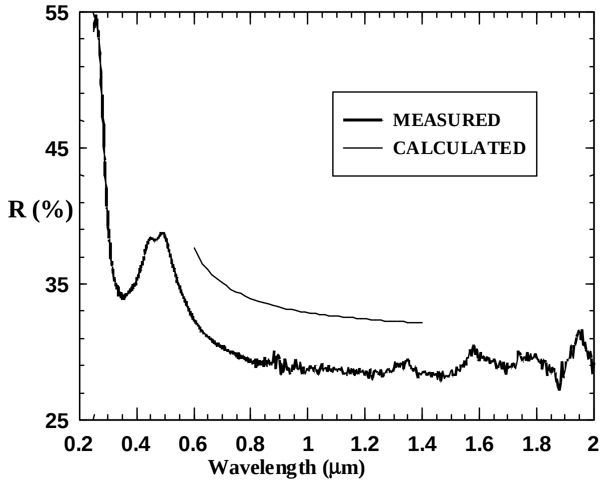

Fig. 6. Calculated and measured reflectance for sample 3.

DISCUSSION OF RESULTS

Due to its atomically smooth surface, sample 1 provided a near-ideal case for this study. The good agreement between the optical parameters of sample 1 to references, and the close correspondence between calculated and measured reflectance, demonstrate the validity of the ellipsometric data, and the subsequent modeling procedure. A detailed knowledge of the properties of the surface oxide would improve the accuracy of the optical model. As an alternative, raw measurements would benefit by etching the sample surface just prior to measurement in a non-oxidizing environment to eliminate the need to consider an oxide [6].

Lower values of measured reflectance, compared to calculated reflectance, were observed for samples 2 and 3. This observation was most apparent in the sample with the roughest surface, sample 3. It should be noted that the large surface roughness affected both the ellipsometric and the reflectance measurements. Reflectance measurements are more affected by roughness, on the order of the wavelength, than ellipsometric measurements due to scattering. A specular sample, therefore, would be expected to give more accurate results both for the determination of the optical constants and for a comparison between calculated and measured reflectance.

Modeling results for samples 2 and 3 did not show distinct differences in the optical parameters n(λ) and k(λ) for the two samples, as was implied by the differences in their reflectance measurements. It is clear that the modeling needs to be improved to account for the large surface roughness shown by the AFM measurements.

FUTURE WORK

This work represents a preliminary study of the optical properties of $Ga_xIn_{1-x}As$ alloys suitable for TPV converter applications; future work will focus on improved results. A wider range for the ellipsometric measurements is desirable, especially in the area of the critical points and closer to the bandgap for the LMM samples. The determination of the optical constants of the LMM samples would be significantly improved by beginning with a smooth sample, and by knowing the layer thicknesses accurately.

ACKNOWLEDGMENTS

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REFERENCES

[1] M. W. Wanlass, et al., “$Ga_xIn_{1-x}As$ Thermophotovoltaic Converters,” *Solar Energy Materials and Solar Cells*, **41/42**, 1996, pp. 405-17.

[2] P. Bhattacharya, ed., *Properties of Lattice-Matched and Strained Indium Gallium Arsenide*, INSPEC EMIS Datareviews Series, Short Run Press, Ltd., Exeter, UK, 1993, p. 7.

[3] R. M. A. Azzam, and N. M. Bashara, *Ellipsometry and Polarized Light*, Chapter 4, North-Holland Publishing, 1977.

[4] *Film Wizard Optical Thin Film Software Instruction Manual*, Chapter 5, Scientific Computing International, Encinitas, CA.

[5] R. W. Collins, and E. A. Irene, “Optical Properties of Solids,” *Fundamentals of Ellipsometry--Short Course Instruction Manual, Part II*, Materials Research Society, Spring 1995.

[6] G. Horner, “Determination of III-V Semiconductor Constants and Their Use in High Efficiency Solar Cell Optimization,” Masters Thesis, Colorado School of Mines, 1991.

[7] *Film Wizard Software*, Materials file, Scientific Computing International, Encinitas, CA.

[8] E. D. Palik, *Handbook of Optical Constants of Solids*, Academic Press, 1985, p. 439, and p. 486.